From Kraft Pulp Fibers to Si-O-C Ceramics *via* Sol-Gel Synthesis: A Preliminary Study of the Impact of Functionalization and Pre-Pyrolysis

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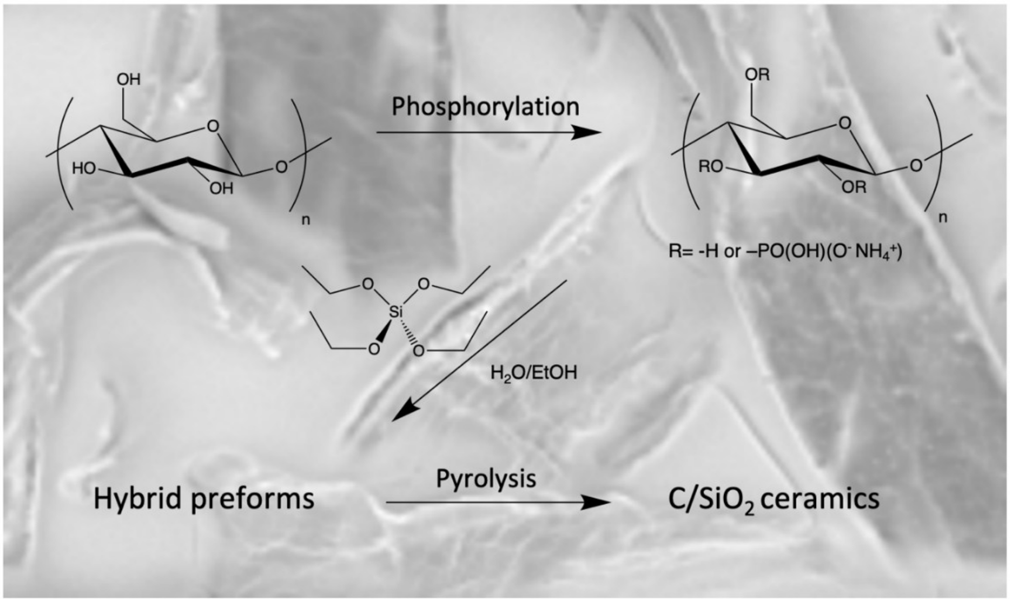
GRAPHICAL ABSTRACT



From Kraft Pulp Fibers to Si-O-C Ceramics *via* Sol-Gel Synthesis: A Preliminary Study of the Impact of Functionalization and Pre-Pyrolysis

Thomas Laporte ,[a] François Brouillette ,[b] Sylvie Foucaud,[a]
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This preliminary study investigated the fabrication of C/SiO_2 ceramics using kraft pulp fibers (KF) and phosphorylated kraft pulp fibers (PKF) impregnated with a ceramic precursor *via* a sol-gel route. The rheological behavior coupled to infrared spectroscopy of the ceramic precursor was examined to optimize the drying process of the impregnated preforms. Thermo-gravimetric analysis and scanning electron microscopy were used to study the thermal behavior and micro-structure of the ceramics. The PKF exhibited a superior thermal stability, and enhanced fiber/ceramic interactions compared to untreated KF. The impact of the fiber functionalization and of the pre-pyrolysis of PKF on fiber/ceramic interactions was also explored. The *in-situ* formation of carbon fibers during heat treatment from PKF appears to be a more effective approach for developing future environmentally sustainable ceramic matrix composites (CMCs).

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Keywords: Kraft pulp fibers; Functionalization; Phosphorylation; Sol-gel process; Fiber/ceramic interaction

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INTRODUCTION

Ceramic matrix composites (CMC) are emerging as a promising choice for the development of advanced, lightweight, and thermo-mechanically efficient materials. However, traditional carbon reinforcements from petroleum sources do not meet eco-friendly standards (Bailey *et al.* 1990). Natural wood fibers represent a sustainable alternative, offering low density, high specific modulus, and suitable strength. Among natural fibers, lignocellulosic fibers, derived from wood, are favored for specialized applications such as the reinforcement of composite materials (Ferdous *et al.* 2021), especially because their production is based on an already highly developed pulp and paper industry.

Recent studies have investigated the development of bio-sourced carbon-reinforced CMC derived from lignocellulosic fibers (such as raw wood, paper, or cellulose nanofibers) with either a ceramic suspension or a polymeric ceramic precursor, using the Polymer-Derived Ceramics (PDCs) route (Zollfrank *et al.* 2004; Hudelja *et al.* 2022). Two key challenges that limit the development of such materials are the discrepancy in thermal degradation resistance between natural fibers and ceramics, and the weak interfacial bonding between carbon fibers and the ceramic matrix (Li *et al.* 2022).

Functionalized cellulosic fibers, particularly phosphorylated kraft pulp fibers (PKF), offer a promising solution to modulate fiber/ceramic interactions, as demonstrated in previous work (Bernard *et al.* 2020). Using a PDCs route, the resulting material behaves similarly to a CMC. Indeed, it is possible to generate carbon fibers within the ceramic matrix, and the interactions between functionalized fibers and the preceramic precursors play key roles in this approach. Moreover, a pre-pyrolysis treatment of the fibers could also be used to modify these interactions and to create the carbon template that would be impregnated in a further step. In this way, and to evaluate this strategy with phosphorylating fibers, this study proposes the development of a sustainable C/SiO_2 ceramic system derived from PKF, impregnated with a polysiloxane synthesized from tetraethyl orthosilicate (TEOS) *via* the sol-gel process, using a more eco-friendly chemical approach. Indeed, ceramic precursors such as allyl-hydridopolycarbosilanes (AHPCS) employed in the PDCs route often require toxic solvents, such as toluene, for their synthesis or cross-linking processes. Reliance on TEOS, on the other hand, enables the synthesis of polysiloxane using a water/ethanol mixture. In this preliminary work, the effects of the fiber functionalization and pre-pyrolysis on fiber/ceramic interactions were examined for the first time. One of the goals of this original study was to elucidate the role of the functionalization by phosphorylation of the fibers on the generated ceramics. For this purpose, a rheological study of the ceramic precursor was conducted to optimize the impregnation process of the fibrous preform. Subsequently, the thermal behavior of the impregnated systems was analyzed using thermogravimetric analysis (TGA). Scanning electron microscopic (SEM) imaging was employed to examine the microstructures of the systems obtained after heat treatment.

EXPERIMENTAL

Functionalized PKF Sheet

The cellulose substrate, KF, is a bleached softwood kraft pulp, provided by a North-eastern Canada pulp and paper mill. The phosphorylation of KF was performed with a phosphate ester (PE) in molten urea (99%, Alfa Aesar) following the method described by Shi *et al*. (2015). The impregnated fibers were heated under a slight vacuum for 3 h at 150 °C. The cellulose, phosphorylating reagent and urea molar ratio was 1:3:17. PE and urea were placed in a crystallizing dish and put in a vacuum oven until the mixture was totally melted. Ground KF was added to the mixture and the impregnated fibers were heated under a slight vacuum for 3 hours at 150 °C. The modified fibers were then washed with deionized water until the filtrate was clear, and then it was dried overnight at 60 °C. Paper sheets (60 $g.m^{-2}$) were formed according to TAPPI/ANSI T 205 (2018) standard method and cut into 1 cm × 1 cm samples, each weighing approximately 20 mg.

Fabrication of Ceramic Systems

The ceramic fabrication procedure is outlined in Fig. 1. The ceramic precursor was synthesized by hydrolyzing TEOS ($Si(OC_2H_5)_4$, 99%, Sigma-Aldrich) with ethanol (EtOH, 96%, Commercial Alcohols) and deionized water, following the method of Jiang *et al.* (2022). The molar ratio of TEOS: EtOH: H_2O was 1: 1.3: 6.2. The pH of the solution was maintained at 2 with 0.1M HCl and the temperature was set to 60 °C for 20 min. The resulting ceramic precursor contained polysiloxane, residual water, and ethanol. Paper preforms were impregnated by deep coating and dried at 60 °C (Fig. 1). Paper preforms were impregnated with this ceramic precursor by dip coating for 5 s, and then dried at 60 °C for 30 min (Fig. 1.). An approximate mass ratio of 40/60 (fibers/ceramic precursor) was obtained for the impregnated preforms. These were pyrolyzed following the thermal cycle described in a previous study (Bernard *et al.* 2020), yielding ceramic systems that is identified as C_KF (from KF) and C_PKF (from PKF). Some PKF samples were also pre-pyrolyzed (PKF.pyr), following the same thermal cycle, and then impregnated with the ceramic precursor to lead to C_PKF.pyr.

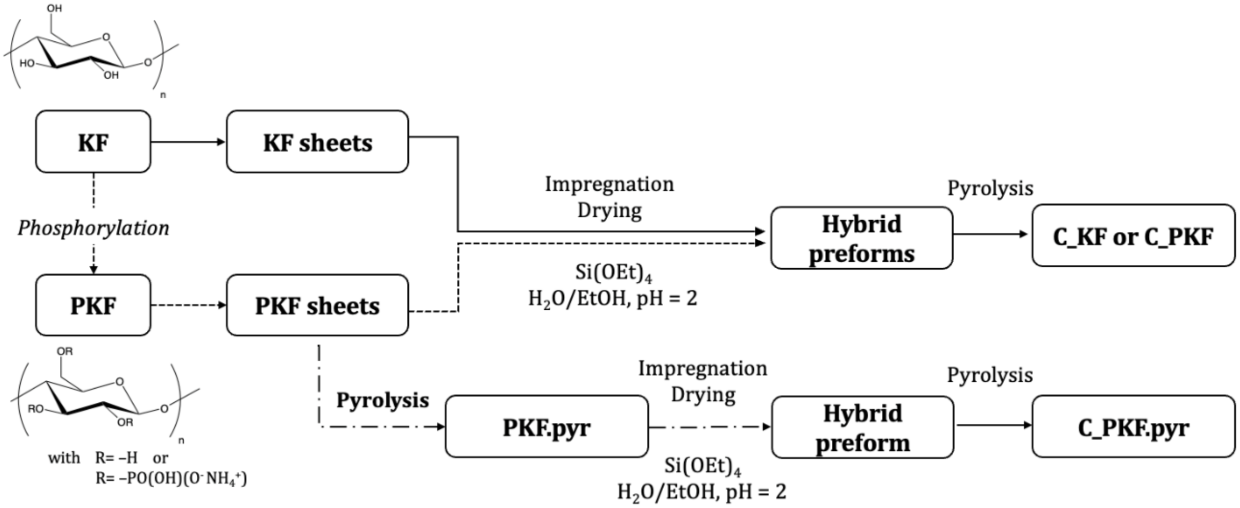

Fig. 1. Different steps to produce C/SiO$_2$ systems

Characterization

The rheological behavior of the ceramic precursor was analyzed using a rotational rheometer (Haake Mars III, ThermoScientific, RheoWin software) with a 35 mm plate-plate geometry. The experiment was conducted over 2 h at 60 °C, with a strain amplitude of $\gamma_0 = 0.1$ to ensure a linear regime of oscillatory deformation at 1.0 Hz. The ceramic precursor was placed between the plates at room temperature. The rheometer was coupled to a Fourier transform infrared (FTIR) spectrometer (Nicolet IS10, ThermoScientific, OMNIC software) in attenuated total reflectance (ATR) mode. Two acquisitions were made over a wavenumber range of 600 to 4000 cm^{-1}, with 16 scans per acquisition and 1.0 cm^{-1} resolution. The thermal behavior of the ceramic precursor gel and impregnated paper preforms was studied by TGA (STA449F3-Netzsch 1400 °C, argon flow: 20 mL.min^{-1}) following the thermal cycle found in Fig. 3. The ceramics microstructure was observed using SEM (Hitachi SU1510, coupled with an Oxford X-max 20 mm^2 detector).

RESULTS AND DISCUSSION

Rheological Behavior of the Ceramic Precursor

To ensure that the ceramic precursor remained retained within the impregnated fibers, its rheological behavior was studied to determine the optimal drying time. The measurements for tetraethyl orthosilicate (TEOS) hydrolysis are performed at 60 °C under air to improve the reaction kinetics.

The rheology curve (Fig. 2a) of the sol-gel polymerization can be divided into three domains. Between domains I and III, the complex viscosity ($|\eta^*|$) increased by a factor of 105. The elastic (G') and viscous (G'') moduli closely followed the $|\eta^*|$ curve. After 15 min, G' significantly exceeded G'' by roughly one order of magnitude, confirming solidification, and both moduli and $|\eta^*|$ remained constant after 20 min.

Cross-linking began around 10 min, while FTIR analysis (Fig. 2b) reveals the onset of polymerization around 7 min. A decrease in the Si-OH bending band intensity (880 cm^{-1}) and an increase in the Si-O-Si bands intensity (940 cm^{-1} and 790 cm^{-1}) indicate the formation of silicate bridges. Thus, using a drying for 20 min at 60 °C allows the gel to be cohesively incorporated inside the porous architecture and to prevent a flow through the fibers.

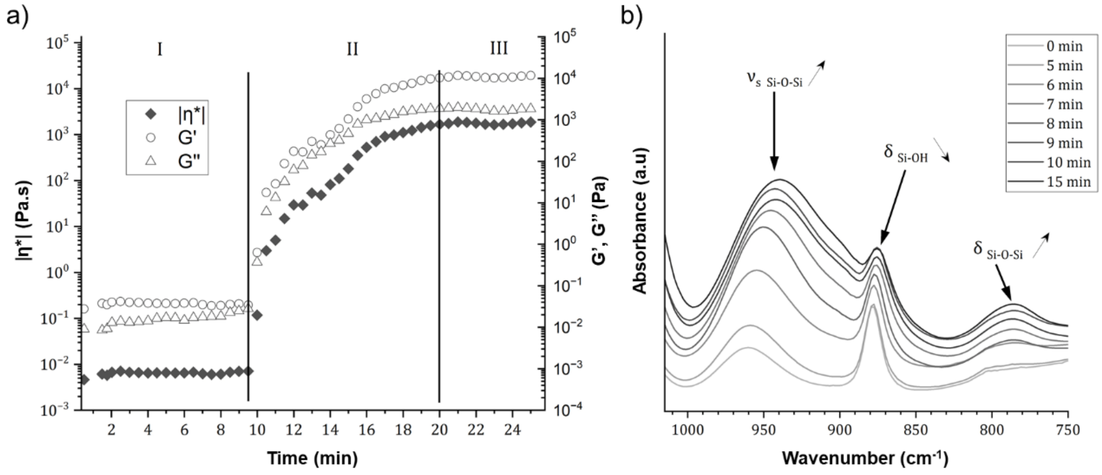

Fig. 2. Rheo-FTIR results at 60 °C: plot of the complex viscosity ($|\eta^*|$), elastic (G'), and viscous moduli (G'') as a function of the time (a), and the associated FTIR curves (b)

Thermal Behavior of Impregnated Preforms

The thermal behavior of the dried impregnated preforms and the ceramic precursor gel is shown in Fig. 3. The dried ceramic precursor gel exhibited a very high mass yield of over 94%. Its mass loss below 150 °C was mainly attributed to the evaporation of free water and residual ethanol.

The thermal behavior of impregnated paper preforms was similar to impregnated fibers, as already discussed in a previous work (Bernard *et al.* 2020). A higher mass yield was observed for impregnated modified fibers sheets (72% for PKF compared to 57% for KF).

As previously noted, an earlier degradation of impregnated PKF was observed, at 200 °C, which has been attributed to a char formation responsible for the flame-retardant character of phosphorylated cellulose (Shi *et al.* 2015). Phosphorylation appears to be an interesting way to limit the decomposition of bio-sourced carbon fibers within the ceramic.

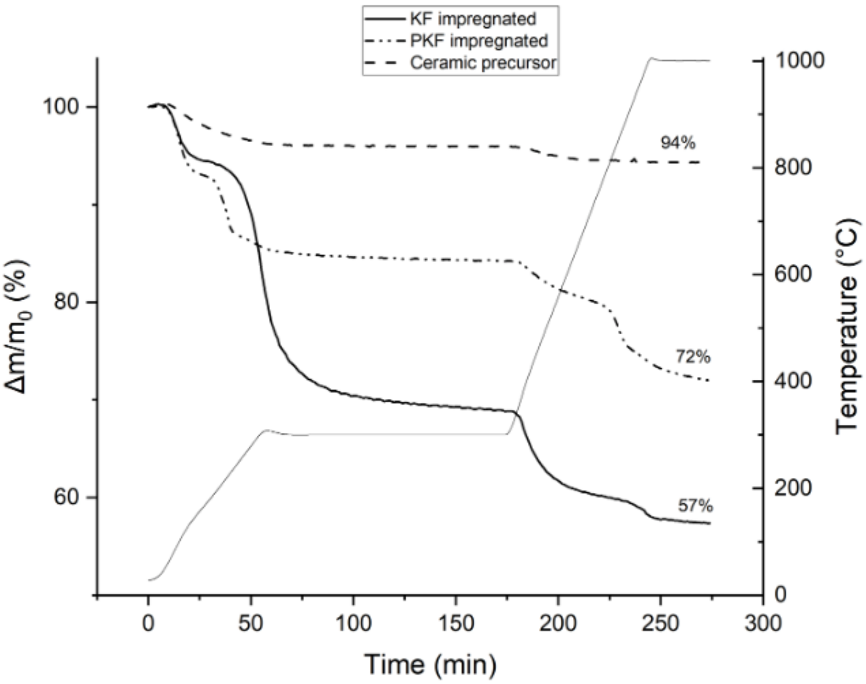

Fig. 3. TGA of KF and PKF impregnated by the ceramic precursor

Morphology of Ceramic Systems

SEM images indicate the influence of fiber functionalization on fiber/ceramic interactions. The images of C_KF (Figs. 4a and 4b) show cross-sectional views, as a ceramic layer had formed on the top of the sample. In C_PKF images (Figs. 4c and 4d, top views), the fibers had become entrapped in the ceramic. In C_KF, a slight detachment of the ceramic from the fibers seems to have occurred, with longitudinal cracks along the fibers. Indeed, conversion of cellulose to carbon entails the loss of material, and so it is reasonable to expect gaps to appear in the structure due to the receding carbon-based part of the composite. In C_PKF, fewer cracks were observed, and longitudinal cracks were not present along the fibers. The ceramic conformed perfectly to the PKF surface, with cracks only perpendicular to the fibers. These cracks may result from differences in thermal expansion between the lignocellulosic fibers, bio-carbon fibers, and the ceramic, or from shrinkage of the pre-ceramic gel during drying (Takahashi and Takenaka 1982; Ding *et al.* 2023). It is worth noticing that fiber/ceramic interactions were enhanced with PKF.

To avoid mechanical stresses or porosity caused by organic species evolution from the fibers during heat treatment, PKF.pyr were used to obtain C_PKF.pyr images (Figs. 4e and 4f). A poor adhesion was observed between the carbon fibers and the ceramic, with cracks forming around PKF.pyr, dislodging them from the ceramic. Thus, pre-pyrolysis weakened fiber/ceramic interactions in C_PKF, as previously reported for pre-pyrolyzed wood fibers and TEOS-derived ceramic matrices (Qian *et al.* 2004). Enhancing interfacial interactions requires increasing the maximum heat treatment temperature above 1470 °C to form a SiC interface *via* a carbothermal reduction. *In-situ* formation of carbon fibers from PKF in the ceramic appears preferable for developing future CMCs at lower temperatures.

Future studies could explore the impact of varying pyrolysis temperature or atmosphere on PKF/ceramic interactions, opening the way to the potential development of environmentally sustainable CMCs.

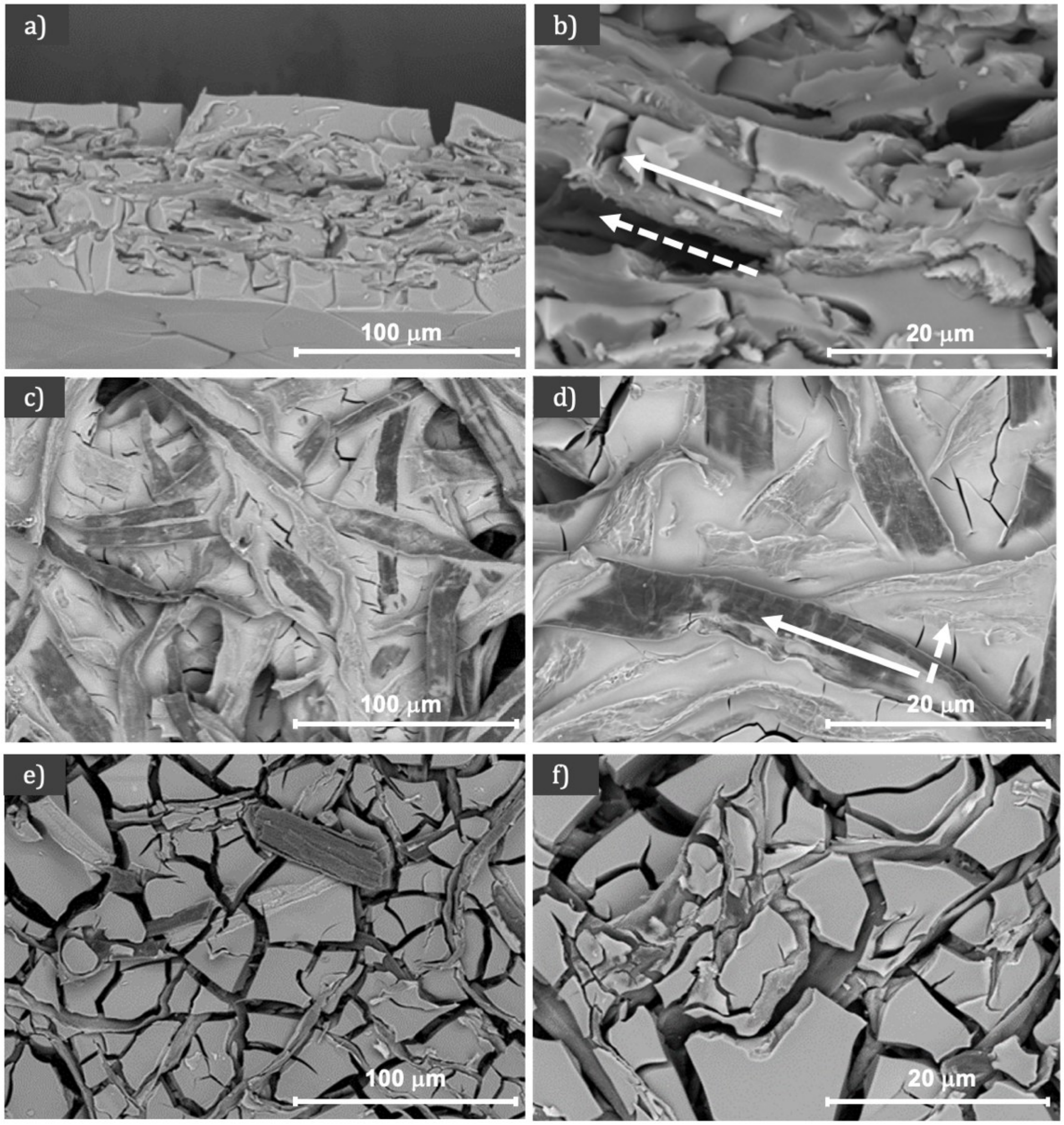

Fig. 4. SEM images of C_KF (a, b), C_PKF (c, d), and C_PKF.pyr (e, f) after pyrolysis. The solid arrow represents the fiber direction, while the dashed arrow indicates the crack direction.

CONCLUSIONS

1. A C/SiO_2 ceramics system was synthesized using kraft pulp fibers (KF) and phosphorylated kraft pulp fibers (PKF) impregnated with a ceramic precursor.
2. Rheological analysis confirmed the rapid gelation of the ceramic precursor at T = 60 °C, allowing for a rapid drying of the impregnated fibers (more than 20 min for a complete solidification, $G' > G''$ with one order of magnitude). Coupling rheological data with FTIR curves, a "lag time" of 3 min between polymerization and cross-linking of the ceramic precursor was observed.
3. The PKF exhibited superior thermal stability (+15% of $\Delta m/m_0$ at 1000 °C) than KF, and enhanced fiber/ceramic interactions compared to untreated KF. Furthermore, pre-pyrolysis of the fibers weakened these interactions, reducing fiber/ceramic bonding. Therefore, the *in-situ* formation of carbon fibers during heat treatment from PKF was judged to be a more effective approach to improve fiber/ceramic adhesion.
4. Future studies could explore the impact of varying pyrolysis temperature or atmosphere on PKF/ceramic interactions, and also evaluating the possibility of performing hydrothermal treatments, thereby opening the way to the potential development of environmentally sustainable CMCs.

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APPENDIX

Sample Photos

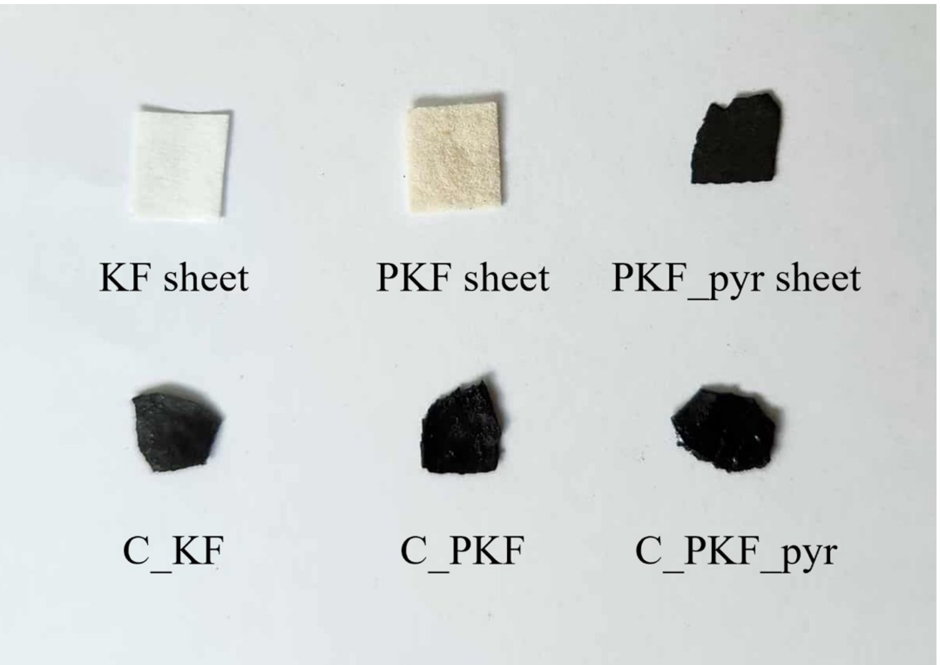

Fig. A1. Photos of the different samples

Chemical Characterization of C_PKF

EDX Analysis

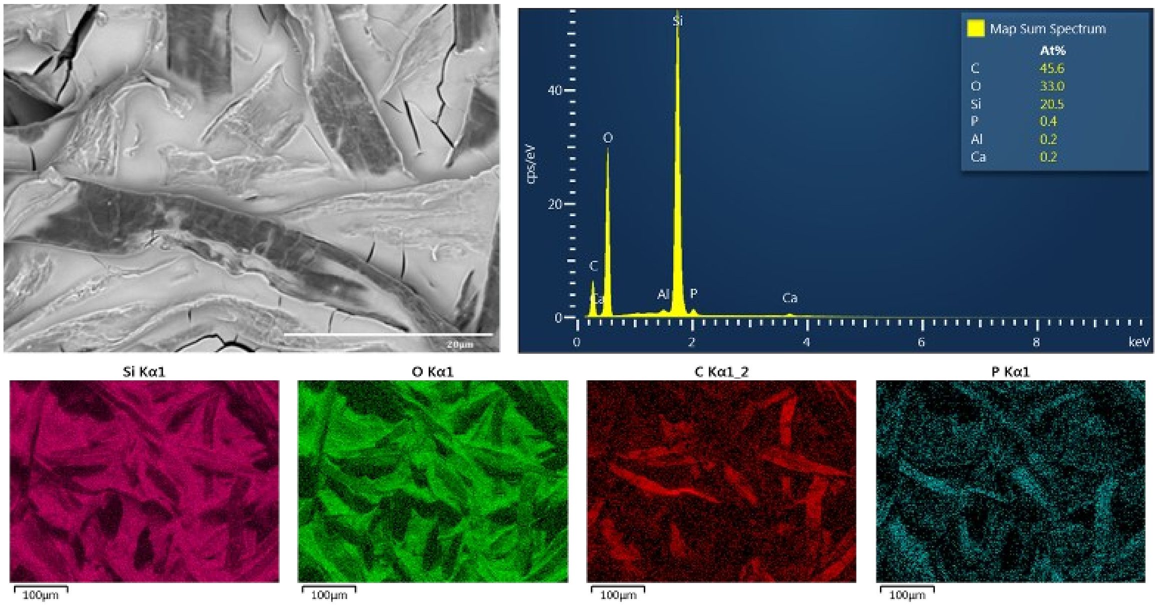

Fig. A2. EDX mapping of **C_PKF** (from Fig 4d)

FTIR Analysis

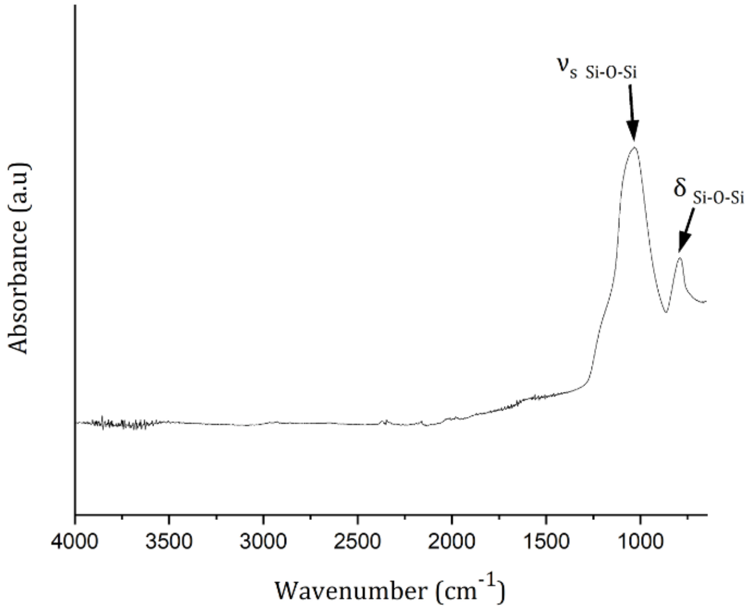

Fig. A3. FTIR spectrum of C_PKF

XPS Analysis

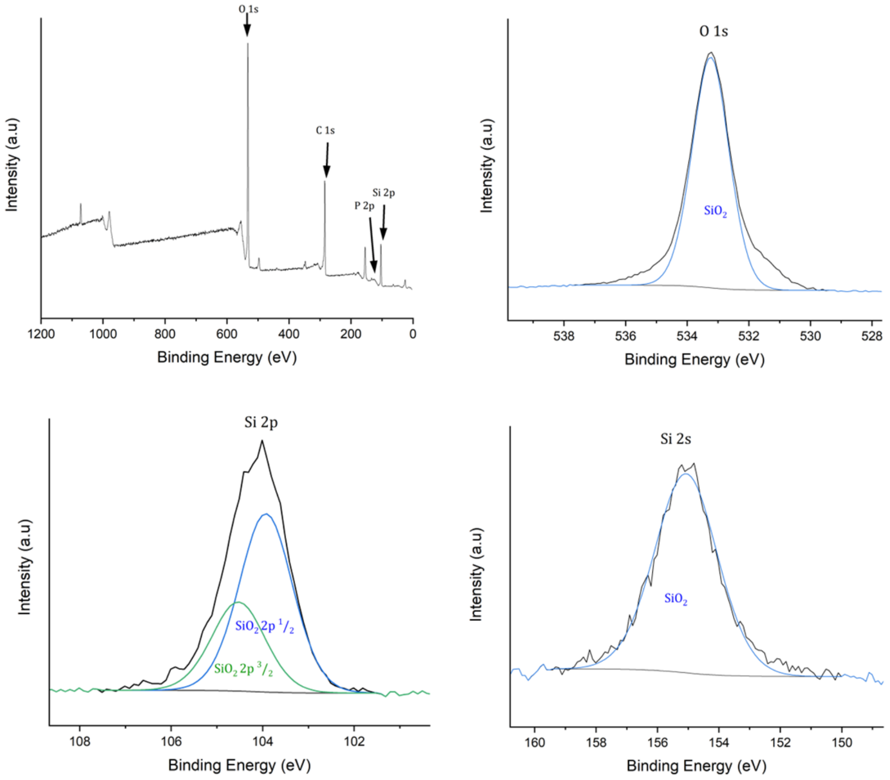

Fig. A4. XPS spectra of C_PKF

Typical XRD Diffractogram of the Pyrolyzed Ceramics

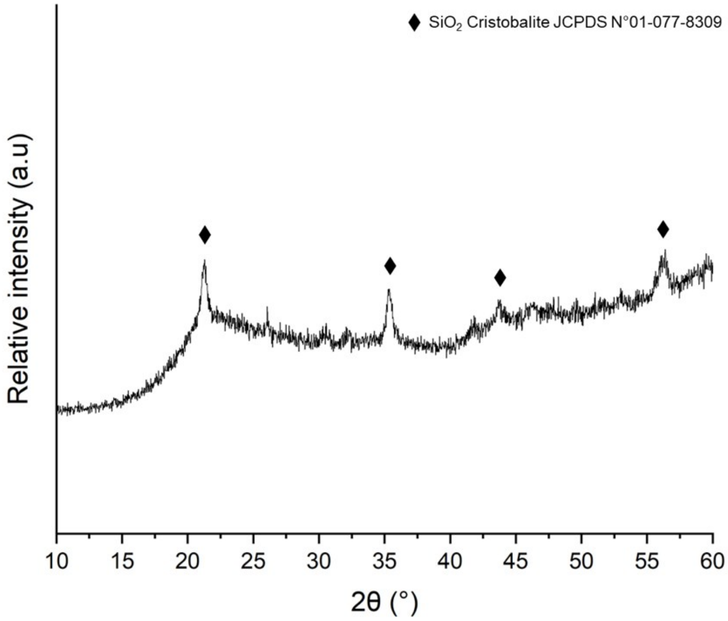

Fig. A5. X-ray diagram of C_PKF

ABBREVIATION LIST

Table A1. List of Abbreviations Used in this Paper

Abbreviation	Definition
AHPCS	Allyl-HydridoPolyCarboSilanes
ATR	Attenuated Total Reflectance
CMCs	Ceramic Matrix Composites
C_KF	Ceramic systems from KF
C_PKF	Ceramic systems from PKF
C_PKF.pyr	Ceramic obtained from pyrolyzed PKF
FTIR	Fourier Transform InfraRed
KF	Kraft pulp Fibers
PDCs	Polymer-Derived Ceramics
PKF	Phosphorylated Kraft pulp Fibers
PKF.pyr	Pyrolyzed PKF
SEM	Scanning Electron Microscopy
TEOS	TetraEthyl OrthoSilicate
TGA	ThermoGravimetric Analysis